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Viewpoint

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Importance of Solvation for the Accurate Prediction of Oxygen Reduction Activities of Pt-Based Electrocatalysts

Platinum and its alloys are active catalysts for the oxygen reduction reaction (ORR).[1] The origin of their high activity and new directions for their enhancement have been provided in terms of their surface electronic properties,[2] adsorption energies of key intermediates,[1b,c,3] and geometric configurations.[1a,4] The most widely used descriptor for the ORR activity of Pt-based materials is the differential adsorption energy of *OH with respect to Pt(111).[1a,b] There is broad agreement on the fact that the optimal catalysts should bind *OH ~ 0.10−0.15 eV more weakly than Pt(111), as confirmed by numerous experiments.[1,3a,b,4]

To obtain such a specific and useful criterion for materials screening, some approximations have to be made, among which we highlight the assumption of identical solvation of the ORR adsorbates (e.g., *O, *OH, and *OOH) on all Pt-based catalysts, independent of the lattice constant and alloying elements present in the structure. Solvation is therefore regarded as an adsorbate-dependent but structure- and composition-independent correction. In this computational study, we show that this assumption is suitable for the analysis of overall trends but should be considered cautiously when aiming to predict the ORR activity of new materials, as the differences in adsorbate solvation energies can be significant, particularly for *OH.

Figure 1 shows the systems under study. Although we consider the explicit solvation of *OH and *OOH embedded in a water bilayer, a common practice in computational catalysis and surface science,[3a,c,5] implicit solvation approaches are also plausible alternatives.[6] To evidence the effect of alloying metals on adsorbate solvation, we have studied Pt(111) and its near-surface surface alloys (NSAs) with 8 late transition metals (cyan spheres in Figure 1): Co, Ni, Cu, Rh, Pd, Ag, Ir, Au. Representative adsorption configurations in vacuum for *OH and *OOH at coverages of 1/9 and 1/3 ML (deemed low and high coverages hereon) are shown in Figure 1a,b. For the low adsorbate coverages, we used 3 × 3 (111) cells, whereas $\sqrt{3} \times \sqrt{3}$ R30° (111) cells were used for the high coverages. *OH/*OOH embedded in hexagonal water bilayers at *OH/*OOH coverages of 1/9 and 1/3 ML are presented in Figure 1c,d. Finally, a hexagonal water bilayer is shown in Figure 1e. Oxygen atoms in H_2O and the adsorbates appear in different colors to facilitate their distinction.

The adsorption energies "in vacuum" (Figure 1a,b) are the free energies of the following reactions:

$$* + H_2O(l) \rightarrow {}^*OH + H^+ + e^- \tag{1}$$

$$* + 2H_2O(l) \rightarrow {}^*OOH + 3H^+ + 3e^- \tag{2}$$

the adsorption energies within the water bilayer (Figure 1c,d) are the free energies of

$$n{}^*H_2O \rightarrow (n-1){}^*H_2O + {}^*OH + H^+ + e^- \tag{3}$$

$$n{}^*H_2O + H_2O(l) \rightarrow (n-1){}^*H_2O + {}^*OOH + 3H^+ + 3e^- \tag{4}$$

where $n = 2$ and 6 for $\sqrt{3} \times \sqrt{3}$ R30° and 3 × 3 (111) cells, respectively. The stabilization provided by the aqueous environment, namely the solvation correction, equals $\Delta G_3 - \Delta G_1$ for *OH, and $\Delta G_4 - \Delta G_2$ for *OOH.

Figure 2 provides an overview of all calculated adsorption energies. A single least-squares fit suffices to describe with good accuracy the adsorption-energy trends of *OH and *OOH in vacuum and the water bilayer (the mean/maximum absolute errors, MAE/MAX, are 0.05/0.14 eV). Besides, Figure 2b shows that our data are also well captured by the state-of-the-art trends (unit slope and 3.2 eV offset),[7] although the MAE/MAX increase to 0.12/0.22 eV. The deviations from 1 to 0.69 in the slope have been observed before and attributed to the increasing covalence of the surface−OOH bonds for late transition metals.[6b] Importantly, the MAE/MAX and gray zones in Figure 2 show that the typical level of accuracy of trends-based analyses is, depending on the approximations made, between ±0.1 and ±0.25 eV.

Table 1 compiles the *OH solvation corrections on the NSAs in the two cells/coverages studied. The average solvation corrections on the cells are −0.55 and −0.50 eV, which agree well with the literature.[3c,4b,8] Note that larger *OH coverages result in slightly less negative solvation corrections (~0.05 eV). The small difference could be the result of (i) an actual coverage effect or (ii) the use of two different unit cells ($\sqrt{3} \times \sqrt{3}$ R30°, 3 × 3 (111)) with different k-point grids (8 × 8 × 1, 4 × 4 × 1). For instance, the average adsorption energies of the water bilayers in Figure 1e are 0.11 and 0.14 eV in the $\sqrt{3} \times \sqrt{3}$ R30° and 3 × 3 (111) cells. In any case, we can safely conclude that *OH solvation is relatively insensitive to coverage effects. Table 2 summarizes the solvation corrections for *OOH on the NSAs in the two cells/coverages studied. The average solvation corrections are now −0.28 and −0.44 eV for the 1/3 and 1/9 ML coverage, respectively, and in contrast to *OH, *OOH shows substantially more negative solvation corrections as its coverage decreases. Although the chemical natures of solvent (water) and solute (the adsorbate) determine to a large extent the latter's solvation,[6b] Tables 1 and 2 suggest that adsorbate coverage and subsurface metals also influence the magnitude of solvation corrections, although the subsurface metal is in contact with neither the adsorbates nor the solution.

The implications of our findings for the ORR modeling on Pt-based materials are significant. As mentioned earlier, the ORR optimum is reached by materials that fulfill the following condition:[1b,c,3a,b,4]

$$\Delta G_{OH} - \Delta G_{OH}^{Pt(111)} \approx 0.10 - 0.15 \text{ eV} \tag{5}$$

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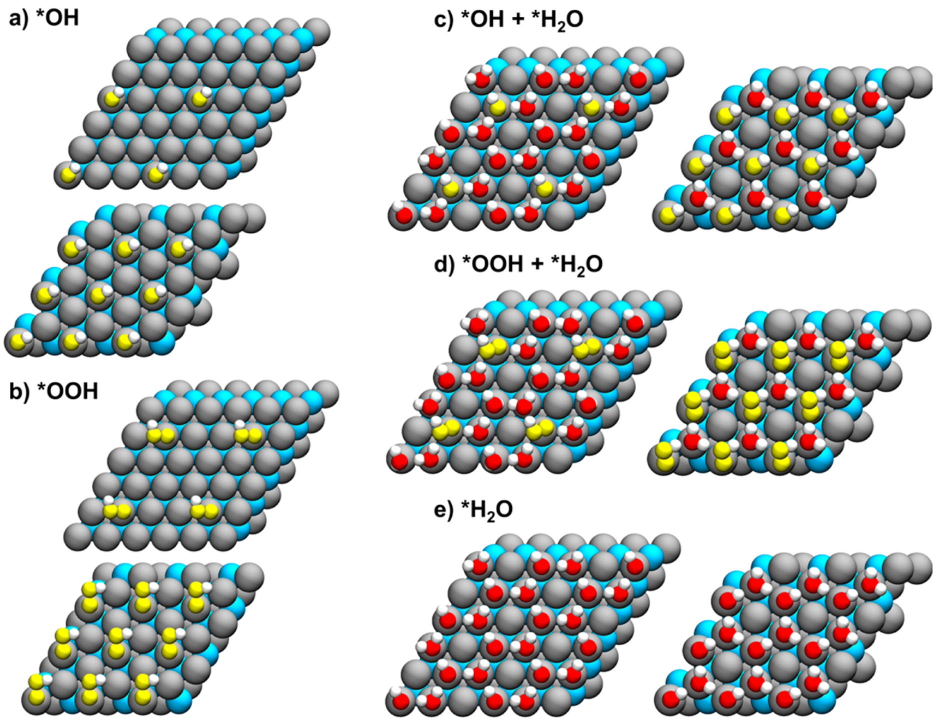

Figure 1. Adsorption in vacuum of (a) *OH, (b) *OOH at coverages of 1/9 (top) and 1/3 ML (bottom). Adsorption in a water bilayer of (c) *OH and (d) *OOH at coverages of 1/9 (left) and 1/3 ML (right). (e) Hexagonal water bilayer on 3 × 3 and $\sqrt{3} \times \sqrt{3}$ R30° (111) cells (left and right). Pt: gray, subsurface metal: cyan, H: white, O in water: red, O in *OH/*OOH: yellow.

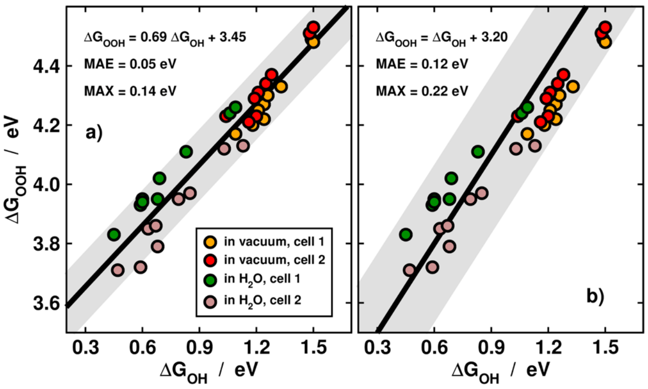

Figure 2. Scaling relations between ΔG_{OH} and ΔG_{OOH}. Cells 1 and 2 are $\sqrt{3} \times \sqrt{3}$ R30° and 3 × 3 (111). In vacuum and in H$_2$O refer to the conditions in Figure 1. (a) Least-squares fit. (b) Fit with slope 1 and 3.20 eV offset.[7] Gray zones including ±2 MAE around the fits are provided. MAE/MAX: mean/maximum absolute errors.

Since the optimal binding is close to that of Pt(111), a slight weakening of 0.10−0.15 eV suffices to reach the optimum. Among other things, to make such prediction the model assumes that the solvation corrections for *OH and *OOH are identical for Pt and its alloys exposing a Pt overlayer.[1b,c,3a,b,4b] Tables 1 and 2 allow us to scrutinize this assumption: *OH solvation corrections can differ by 0.21−0.24 eV, depending on the adsorbate coverage. Extrapolating the *OH solvation correction for Pt(111) to the alloys produces errors up to 0.18−0.21 eV. For *OOH the deviations are smaller, though the corrections can differ by 0.12−014 eV, and extrapolating from Pt(111) causes errors up to 0.11 eV.

While we do not intend to analyze or make particular ORR activity predictions, Tables 1 and 2 suggest that it is not recommendable to assume constant solvation for materials that (nearly) fulfill eq 5. This is because the difference between Pt(111) and the optimal material is only 0.10−0.15 eV, whereas the error associated with identical solvation can be as large as 0.24 eV. This points toward the need for error bars around DFT-based predictions, as errors may originate from the choice of exchange-correlation functional,[9] ion-electron description,[10] and the thermodynamic/kinetic models themselves.[11] Figure 3 shows that the adsorption energies of *OH (top) and *OOH (middle) in the two cells, in vacuum and within the water bilayer, generally become less negative as the number of valence electrons of subsurface metals increases, in line with previous

Table 1. Solvation Corrections (in eV) for *OH on Pt NSAs at Two Coverages[a]

NSA	$\sqrt{3}\times\sqrt{3}$ R30° (111), θ_{OH} = 1/3 ML	3 × 3 (111), θ_{OH} = 1/9 ML
Pt−Co	−0.65	−0.57
Pt−Ni	−0.57	−0.46
Pt−Cu	−0.43	−0.44
Pt−Rh	−0.61	−0.52
Pt−Pd	−0.55	−0.53
Pt−Ag	−0.41	−0.37
Pt−Ir	−0.64	−0.57
Pt−Pt	−0.58	−0.57
Pt−Au	−0.49	−0.43
average	−0.55	−0.50
range	0.24	0.21
LNDA	−0.10	−0.08
LPDA	0.14	0.13
LNDPt	−0.06	0.00
LPDPt	0.18	0.21

[a] Range: difference between the maximal and minimal values in the list. LPDA/LPDPt: largest positive deviation from the average/Pt−Pt. LNDA/LNDPt: largest negative deviation from the average/Pt−Pt.

Table 2. Solvation Corrections (in eV) for *OOH on Pt NSAs at Two Coverages[a]

NSA	$\sqrt{3}\times\sqrt{3}$ R30° (111), θ_{OOH} = 1/3 ML	3 × 3 (111), θ_{OOH} = 1/9 ML
Pt–Co	−0.34	−0.45
Pt–Ni	−0.28	−0.39
Pt–Cu	−0.25	−0.39
Pt–Rh	−0.30	−0.43
Pt–Pd	−0.27	−0.44
Pt–Ag	−0.23	−0.40
Pt–Ir	−0.34	−0.53
Pt–Pt	−0.26	−0.49
Pt–Au	−0.22	−0.40
Average	−0.28	−0.44
Range	0.12	0.14
LNDA	−0.07	−0.09
LPDA	0.05	0.05
LNDPt	−0.08	−0.03
LPDPt	0.04	0.11

[a] Range, LPDA/LPDPt, LNDA/LNDPt are defined in Table 1.

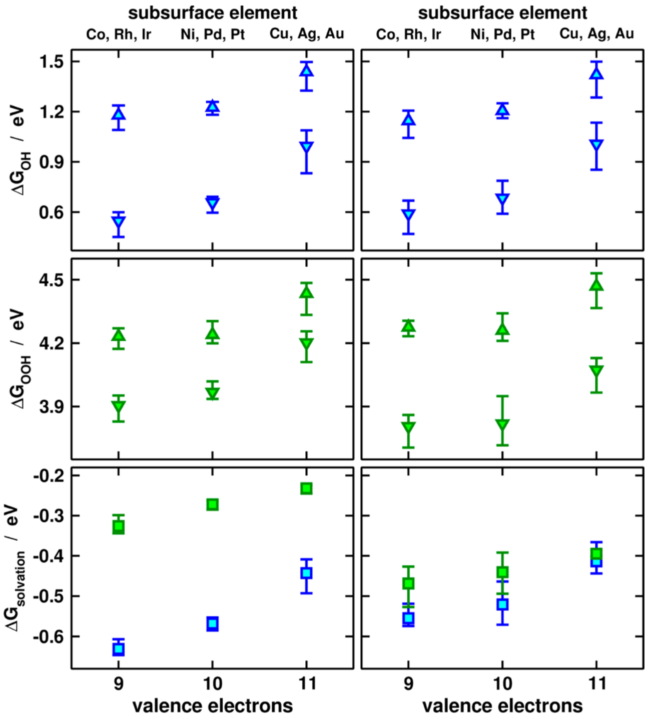

Figure 3. Adsorption-energy trends for *OH (top) and *OOH (middle) on NSAs as a function of the number of valence electrons of subsurface metals on the $\sqrt{3}\times\sqrt{3}$ R30° (left) and 3 × 3 (111) (right) cells. Bottom: solvation corrections (■) for *OH/*OOH (blue/green), calculated as the difference between the data in the top and middle panels in vacuum (▲) and the water bilayer (▼).

adsorption-energy trends reported for NSAs.[12] As a result, solvation corrections follow similar trends, and one can devise per-subsurface-metal-group corrections with maximum errors of ±0.05 eV, as shown in Figure 3 (bottom).

We note that there is growing interest in solvation in the computational electrocatalysis community,[6a,c,8] and various water structures on Pt surfaces have been elucidated.[5,13] Moreover, it was recently shown that interfacial water configurations modify hydrogen evolution rates on Pt(111).[14] For the ORR, future studies should ascertain how much of the experimental enhancement displayed by Pt alloys is due to solvation in addition to ligand[3b] and strain effects.[1c,3a] Possibly, as predicted theoretically,[6b,d] engineering surface solvation can help design better ORR electrocatalysts.

In summary, in this computational study we have shown that constant solvation for Pt and its alloys is a suitable approximation for the analysis of overall ORR trends. However, predicting new Pt-based materials requires a higher level of refinement in which *OOH and especially *OH solvation should be calculated at appropriate coverages, and per-subsurface-metal corrections are recommendable.

■ METHODS

The calculations were made with VASP[15] using PBE,[16] a plane-wave cutoff of 450 eV, and the conjugate gradient method. Further details are provided in the Supporting Information.

Zheng-Da He[†,‡]
Selwyn Hanselman[†]
Yan-Xia Chen[‡]
Marc T. M. Koper[*,†]
Federico Calle-Vallejo[*,†]

[†] Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
[‡] Hefei National Laboratory for Physical Science at Microscale and Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01018

Additional calculation details (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: m.koper@chem.leidenuniv.nl.
*E-mail: f.calle.vallejo@chem.leidenuniv.nl.

ORCID

Marc T. M. Koper: 0000-0001-6777-4594
Federico Calle-Vallejo: 0000-0001-5147-8635

Notes

The authors declare no competing financial interest.

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